Carbohydrate Polymers 96 (2013) 435–439

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Multifunctional finishing of cotton with 3,3′,4,4′-benzophenone tetracarboxylic acid: Functional performance

Aiqin Hou[a,b], Gang Sun[b,*]

[a] National Engineering Research Center for Dyeing and Finishing of Textiles, Donghua University, Shanghai 201620, China
[b] Division of Textiles and Clothing, University of California, Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 2 March 2013
Received in revised form 28 March 2013
Accepted 10 April 2013
Available online 18 April 2013

Keywords:
Chemical modification
Cotton fabric
Wrinkle free
UV protection

ABSTRACT

3,3′,4,4′-Benzophenone tetracarboxylic acid (BPTCA) can directly react with hydroxyl groups on cotton cellulose to form ester bonds, which could crosslink cellulose and provide wrinkle-free functions to the cotton fabrics. BPTCA, as a derivative of photo-active benzophenone, can absorb ultraviolet lights and offer ultraviolet (UV) protective and photo-sensitive functions on the treated materials. Finishing conditions such as agent concentration, curing temperature and time, could affect ester bond formation and crosslinking of cellulose. Wrinkle-free and UV protective functions in relationship to the functional agent, as well as surface morphology of BPTCA treated cotton were investigated as well.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Clothing has been considered and actually has acted in many aspects as a "second skin", a protective outer layer, to human. Real human skin is the largest organ that has various protective functions against almost all natural hazards. When novel protective functions are added onto clothing materials, the new products are imaged as a second skin to wear. Based on general expectations, such clothing materials should at least possess several functional properties including comfort, easy-care, moisture and heat regulating, self-cleaning against biological and chemical toxins, sun or UV-protective functions. For example, cotton fabric is the most popular material used in various consumer and professional apparels due to its comfort, moisture absorbing and excellent wearing properties. Additional wrinkle-free, UV blocking, and antimicrobial properties are considered necessary to be added for human convenience and health demands, which could make the clothing more resemble a second skin. Wrinkle-free treatment of cotton fabrics is generally achieved by chemically crosslinking cotton cellulose by using traditional formaldehyde containing N-methylol compounds or non-formaldehyde 1,2,3,4-butanetetracarboxylic acid (BTCA) (Lam, Kan, & Yuen, 2011; Montazer & Afjeh, 2007; Yang & Wei, 2000a, 2000b). The UV protective function on the fabrics, which is important for protecting both materials and wearers (Gouda & Keshk, 2010; Lu, Fei, Xin, Wang, & Li, 2006), can be obtained by incorporating UV absorbents or UV blockers onto the fabric (Czajkowski, Paluszkiewicz, Stolarski, Kaz′mierska, & Grzesiak, 2006; Hatch & Osterwalder, 2006; Hou, Zhang, & Wang, 2012; Ibrahim, E-Zairy, & Eid, 2010a; Wang & Hauser, 2010). To obtain multiple functions, multi-step chemical treatments of cotton fabrics are normally required, which could consume large quantity of water and energy and consequently increase costs and environmental impacts. Thus, development of energy efficient and multi-functional finishing processes of textiles is extremely important (Ibrahim, Eid, Hashem, Refai, & EL-Hossamy, 2010).

In a previous study, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BPTCD) was employed in a direct reaction with cotton cellulose by using N,N-dimethylformamide (DMF) as a solvent (Hong & Sun, 2011). The reactive anhydride groups can crosslink cellulose and bring durable press and photo-active functions to the fabrics, though the treatment process was not practical due to the use of DMF. In a more recent study, 3,3′,4,4′-benzophenone tetracarboxylic acid (BPTCA), which is hot water soluble, was directly used to react with cellulose without formation of anhydride structures during the treatment process (Hou & Sun, 2013). Such a process is commercially practical, which leads to further evaluation of functional properties, including UV-protection, wrinkle resistance, and more importantly mechanical properties, of the treated fabrics. Surface morphological changes of the treated fabrics were also examined by a scanning electron microscope (SEM). The results indicate that BPTCA could bring multiple functions onto cotton fabrics in a simple one step wet finishing process.

* Corresponding author. Tel.: +1 530 752 0840; fax: +1 530 752 7584.
E-mail address: gysun@ucdavis.edu (G. Sun).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.04.015

2. Experimental

2.1. Materials

Desized, scoured, and bleached cotton plain weave fabrics (#400) were purchased from Test Fabrics Inc. (West Pittston, PA, USA). 3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BPTCD) and sodium hypophosphite monohydrate were purchased from Sigma Chemical Co. (Louis, MO, USA). All other chemicals were purchased from Fisher Scientific (Pittsburgh, PA, USA). All reagents were used as received without any further purification.

2.2. Treatment of cotton fabrics

3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BPTCD) was dissolved in hot water to completely hydrolyze to 3,3′,4,4′-benzophenone tetracarboxylic acids (BPTCA), and the solution was directly applied in a wet finishing process on cotton fabrics. Sodium hypophosphite monohydrate was added as a catalyst to the BPTCA solution in a mole ratio of catalyst:BPTCD = 1:2. The cotton fabric was first impregnated in the solution and then padded through two dips and two nips to reach an average wet pickup of 120%, dried at 90 °C for 3 min, and cured in a curing oven (Roaches International Ltd., England) at a specified temperature for 3 min. And finally the treated fabrics were washed with water and air-dried in a conditioning room (25 °C, 65% R.H.) for 24 h.

2.3. Characterization of treated fabrics

Add-ons of BPTCA on the treated cotton fabrics were obtained by measuring weight changes of the fabrics before and after the treatments. Ultraviolet protection factors (UPF) of the fabrics were measured by using an Ultraviolet Transmittance Fabric Analyzer, UV-1000F (Labsphere Co., USA). Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Electron Co., USA) with a resolution of 4 cm^{-1}, and the measurements were carried out by using KBr pellets.

Wrinkle recovery angle (WRA) and tensile strength of the cotton fabrics were measured according to AATCC Standard Test Method 66-2008 and ASTM Standard Test Method 5035-2006, respectively. Twelve specimens (six for warp and six for filling) were tested for WRA. Ten specimens (five for warp and five for filling) were employed in tensile strength tests on an Instron 5566 (Instron, Norwood, USA).

Washing durability of the fabric functions was evaluated following AATCC Standard Test Method 61-2009 (2A). The fabric used for the washing durability tests was treated with 50 g/L BPTCD, and cured at 160 °C for 3 min. The samples were placed in a Launder-O-meter using an accelerated laundering cycle at 49 ± 2 °C in a detergent solution. Then the fabric samples were washed one, two and three times, respectively. Each accelerated washing is equivalent to five home launderings. The wrinkle properties (WRA) were then evaluated again. The surface morphologies of cotton fabrics were examined using a scanning electron microscope (Philips XL30, USA).

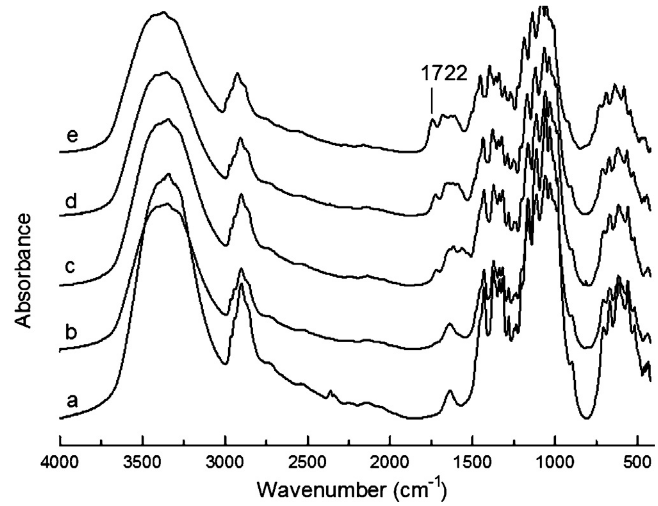


Fig. 1. FTIR spectra of untreated and treated cotton fabrics with different amounts of BPTCD curing at 160 °C for 3 min: (a) untreated (control) cotton fabric; (b) fabric treated with 10 g/L BPTCD; (c) fabric treated with 30 g/L BPTCD; (d) fabric treated with 50 g/L BPTCD; (e) fabric treated with 70 g/L BPTCD.

3. Results and discussion

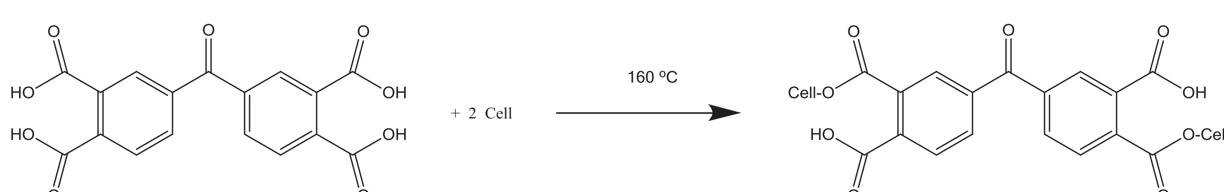
3.1. BPTCA treatment of cotton fabrics

BPTCA was applied onto cotton fabrics by using a two-dip-two-nip wet treatment process. The BPTCA treated fabrics were dried at 90 °C for 3 min to remove water, and cured at an elevated temperature for certain time to accelerate the esterification between the carboxylic acids and hydroxyl groups (Hou & Sun, 2013) shown in Scheme 1.

The structural changes of BPTCA treated cotton fabrics were examined by using FTIR. Fig. 1 shows FTIR spectra of the untreated (control) cotton fabric and the fabrics treated with different concentrations of BPTCA solutions. The peak at 1722 cm^{-1} is a corresponding band of ester bond formed after curing, confirming the direct esterification reaction between BPTCA and cotton cellulose. The intensities of 1722 cm^{-1} band on the cotton fabrics increased with the increase of BPTCA concentration, clearly noticeable in the FTIR spectra and consistent with the results of weight increases of the treated fabrics (Fig. 2).

3.2. Conditions on esterification reaction

The primary goal of this work was to achieve proper crosslinking effects and consequently desired wrinkle-free functions on the BPTCA treated cotton. According to the reaction mechanism discussed in the previous paper (Hou & Sun, 2013), amount of BPTCA in finishing baths and reaction temperature could significantly affect the formation and amount of ester bonds. Thus, different concentrations of BPTCA (10, 30, 50, 70 g/L measured in amount of solid BPTCD) were used to treat the fabrics at selected curing temperatures (140, 160, 170, 180 °C). Increasing BPTCA concentration in the



Scheme 1. Chemical reaction of cellulose with BPTCA.

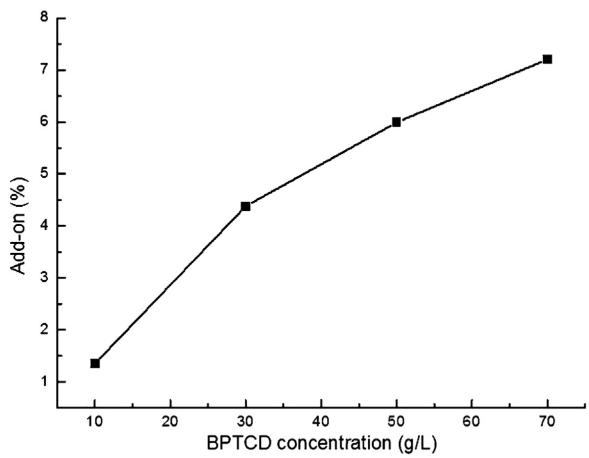


Fig. 2. Effect of concentration on add-on of BPTCA to cotton fabric.

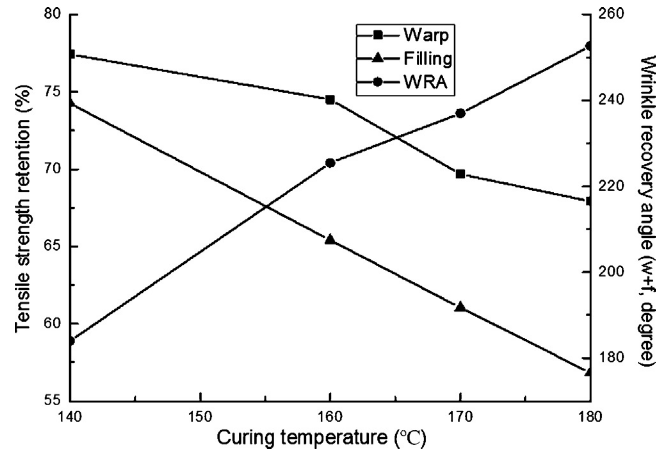


Fig. 4. WRA and tensile strength retention of cotton fabrics treated with 50 g/L BPTCD and cured under different temperatures for 3 min, w: warp; f: filling.

finishing baths could increase the amount of the agent loaded to the fabrics and then increase add-ons of BPTCA to the cotton fabric after curing at an elevated temperature (160 °C). The results, shown in Fig. 2, indicate that as the concentration of BPTCD changing from 30 g/L to 70 g/L, the increase of the incorporated agent was gradual, though the increase was a little more from concentration increase of 10 g/L to 30 g/L. Such an increase is and should be consistent with the intensity increase of the FTIR since this band also covers free carboxylic acid groups on BPTCA. Any increase of the band is coming from the chemical incorporation of BPTCA to cellulose. Based on expectations on desired functional properties, a concentration of 50 g/L was selected to study the temperature impact.

Raising curing temperature could accelerate esterification reaction of acid and hydroxyl groups, possibly improving functional performance of the fabrics as well. However, very high curing temperature could also cause oxidative reactions of cellulose and damage fabric properties. In addition, higher temperature may consumer more energy. The effect of curing temperature on the add-on of BPTCA on the treated cotton is shown in Fig. 3. The curing temperatures lower than 160 °C seem a little less efficient in esterification reaction. Higher than 160 °C the add-on of the agent was only gradually increased.

3.3. Wrinkle recovery and mechanical properties

The above results have demonstrated that BPTCA can form ester bonds with cellulose, but only BPTCA crosslinked cellulose could exhibit wrinkle free functions. Again, the curing temperature may have significant impact on the crosslinking reactions since higher temperature could accelerate esterification reactions as shown in Fig. 3. In order to investigate the effect of curing temperature on wrinkle recovery property, the cotton fabric samples treated with 50 g/L BPTCD and cured at the temperature range of 140–180 °C were also employed in this study. The wrinkle recovery angle (WRA) of the control fabric sample was 154.2°. The effect of the curing temperature on WRA of the treated cotton fabrics are plotted in Fig. 4. The WRA of the treated fabrics increased gradually with the increasing curing temperature, especially from 140 °C to 160 °C, indicating that more crosslinking ester bonds formed at higher temperature. This result reveals that not only more BPTCA was incorporated onto cellulose, but also more crosslinking ester bonds were formed in the fabrics under higher curing temperatures. However, as the WRA values of the fabrics improving, the tensile properties (tensile strength retentions at warp and filling directions) of the treated cotton fabrics decreased dramatically with the increasing curing temperatures (Fig. 4). Due to the fact of strong acidity of a polycarboxylic acid, acid catalyzed degradation of cellulose could be accelerated as well under higher temperature, leading to reduction of tensile strengths in both directions. Considering both wrinkle recovery and tensile strength properties of the fabrics, curing temperature at 160 °C was selected for future large scale tests. Comparing the results shown in both Figs. 3 and 4, it is reasonable to speculate that more grafting of BPTCA onto cellulose occurred at a curing temperature of 140 °C, while higher temperature assisted more crosslinking esterification reaction between BPTCA with cellulose.

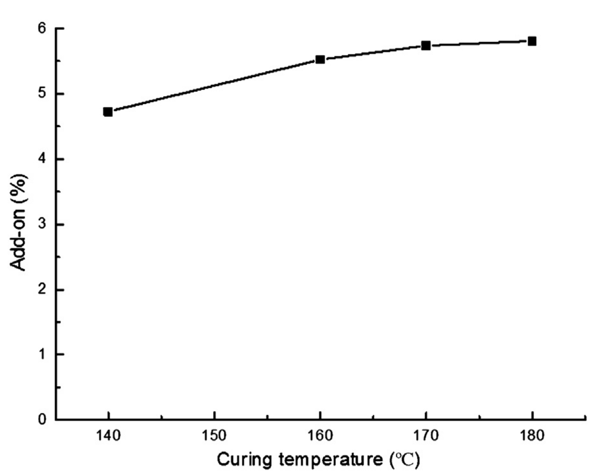


Fig. 3. Effect of curing temperature on add-on of BPTCA to cotton fabric.

After selecting 160 °C as a proper curing temperature for the treatment of the cotton cellulose, varied BPTCD concentrations (10, 30, 50, 70 g/L) were reevaluated under the same temperature. Again, both WRA and tensile retention values of the treated fabrics were measured and are shown in Fig. 5. After consideration of both wrinkle free expectation and proper mechanical properties, a concentration of 50 g/L was a preferred choice, though 30 g/L could be another one if tensile property weighs more over WRA of the fabric.

As a basic requirement of functional textiles, the laundry durability of the properties is very important. A preliminary evaluation of laundry durability of wrinkle recovery angle of the BPTCA (50 g/L) treated fabric was conducted. WRA (w + f) of the original treated cotton fabric without washing was 236°, while after washing one time it changed to 232°. After two and three washings the sample WRA values changed to 233 and 231°, respectively, indicating that the crosslinking between BPTCA and cotton fibers possess excellent laundry durability, consistent with the nature of ester bonds.

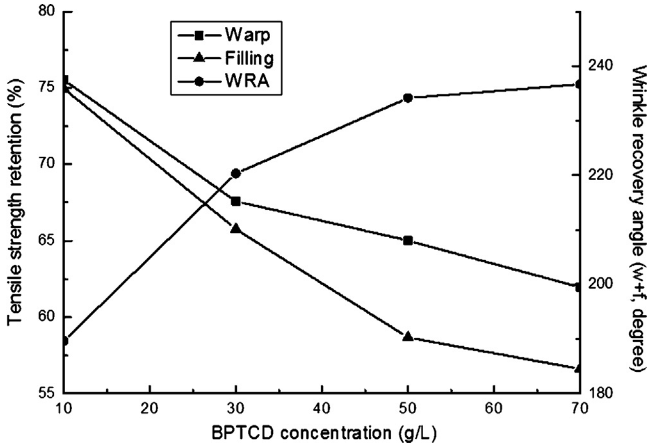


Fig. 5. WRA and tensile strength retention of cotton fabrics treated with different BPTCD concentrations and cured at 160 °C for 3 min.

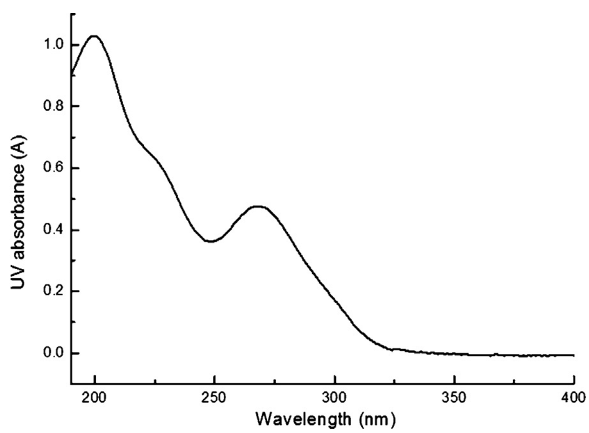


Fig. 6. UV absorption of BPTCA in water.

3.4. UV-protective properties of fabrics

BPTCA, as a derivative of benzophenone, could be a good adsorbent compound to ultraviolet light. The UV absorption spectrum of BPTCA in water is shown in Fig. 6, demonstrating that BPTCA have two strong absorption bands in 190–250 nm and 250–325 nm. Thus, BPTCA treated fabrics should also possess UV protective function.

The radiation of sunlight in the ultraviolet (UV) range (200–400 nm) is subdivided into UV-C (200–280 nm), UV-B (280–315 nm) and UV-A (315–400 nm). Due to absorption of ozone layer in the upper atmosphere, UV-C is filtered. UV radiations reaching to the surface of the earth are mainly UVB and UVA. Ultraviolet protection factor (UPF), Eq. (1), is the measurement of UV protection property of fabrics.

Table 1
UV protection properties of the treated cotton fabrics and control fabric.

Curing temperature (°C)	BPTCD concentration (g/L)	UPF	UV-protection class
Control	0	4.95	No
160	10	27.07	Very good
160	30	55.18	Excellent
160	50	53.42	Excellent
160	70	54.53	Excellent
140	50	52.97	Excellent
160	50	55.97	Excellent
170	50	56.02	Excellent
180	50	67.53	Excellent

$$\mathrm{UPF} = \frac{\int_{290}^{400} E_\lambda \times S_\lambda \times d\lambda}{\int_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times d\lambda} \tag{1}$$

where S_λ is erythema action spectrum, E_λ is solar irradiance, $d\lambda$ is wavelength interval in nm, and T_λ is spectral transmittance of the specimen.

Usually, UPF value of 15–24 is classified as good protection, 25–39 as very good and above 40 as excellent protection against solar UV radiation (Czajkowski et al., 2006). UPF values of the cotton fabrics treated with BPTCD, 50 g/L, cured at different temperatures for 3 min, and treated with different BPTCA concentrations, cured at 160 °C for 3 min were measured. The results are summarized in Table 1. The control sample showed a low UPF value at 4.95. The UPF values of the cotton fabrics treated with BPTCD (50 g/L) and cured at different temperatures all exceeded 50, having excellent UV protection property. At curing temperature 160 °C, the cotton fabric treated with low BPTCD (10 g/L) already showed a very good UPF factor above 27, and when BPTCD concentration was higher than 10 g/L, all the treated cotton fabrics had excellent UV-protective property. It can be seen that BPTCA as a derivative of benzophenone can significantly improve the fabric protective performance against ultraviolet irradiation. The UV protection properties of the treated fabrics are mainly attributed to the benzophenone, which absorbs UV efficiently.

3.5. Surface morphology of fabrics

Surface morphology of the treated cotton fabric was characterized by using scanning electron microscope (SEM), and the images of control and BPTCA treated cotton fibers (BPTCD 50 g/L, cured at 160 °C for 3 min) are shown in Fig. 7(a) and (b), respectively. The image of the treated cotton fibers did not reveal much noticeable changes on the surface compared with the untreated one, indicating that the BPTCA treatment on the cotton did not damage the cotton fiber surface structure. Such a result is consistent with the tensile properties of the BPTCA treated cotton samples, which have

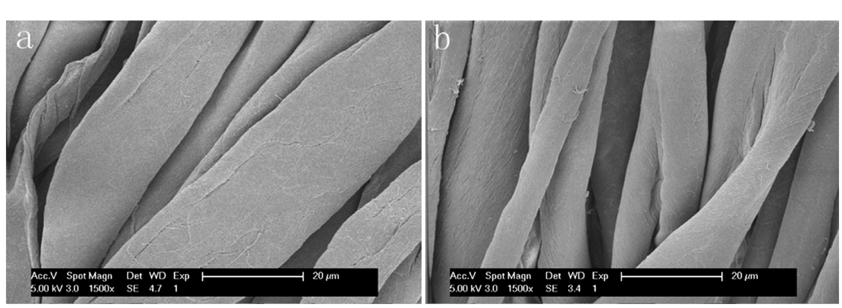


Fig. 7. SEM images of cotton fabrics: (a) control sample and (b) treated sample (50 g/L BPTCD, cured at 160 °C for 3 min).

relatively higher tensile strength retention values than ones treated by BTCA or other polycarboxylic acids (Kang, Yang, Wei, & Lickfield, 1998).

4. Conclusion

BPTCA was able to directly react with hydroxyl groups on cellulose to form ester bonds and crosslinkings. High temperature accelerated the esterification and consequently resulted in more ester bond crosslinking between BPTCA and cotton cellulose. Thus, the BPTCA treated cotton fabrics demonstrated excellent wrinkle recovery properties. In addition, the treated fabrics showed excellent UV protection property due to the addition of benzophenone group, proper mechanical property due to less surface damage to the fibers, and good laundry durability due to the stable covalent ester connections.

Acknowledgement

Dr. A. Hou is grateful for the financial support from Shanghai Municipal Education Commission for conducting research at University of California, Davis.

References

Czajkowski, W., Paluszkiewicz, J., Stolarski, R., Kaz′mierska, M., & Grzesiak, E. (2006). Synthesis of reactive UV absorbers, derivatives of monochlorotriazine, for improvement in protecting properties of cellulose fabrics. *Dyes and Pigments*, *71*, 224–230.

Gouda, M., & Keshk, S. M. A. S. (2010). Evaluation of multifunctional properties of cotton fabric based on metal/chitosan film. *Carbohydrate Polymers*, *80*, 504–512.

Hatch, K. L., & Osterwalder, U. (2006). Garments as solar ultraviolet radiation screening materials. *Dermatologic Clinics*, *24*, 85–100.

Hong, K. H., & Sun, G. (2011). Photoactive antibacterial cotton fabrics treated by 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. *Carbohydrate Polymers*, *84*, 1027–1032.

Hou, A., & Sun, G. (2013). Multifunctional finishing of cotton with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride: Reaction mechanism. *Carbohydrate Polymers*, *95*, 768–772. http://dx.doi.org/10.1016/j.carbpol.2013.02.027

Hou, A., Zhang, C., & Wang, Y. (2012). Preparation and UV-protective properties of functional cellulose fabrics based on reactive azobenzene Schiff base derivative. *Carbohydrate Polymers*, *87*, 284–288.

Ibrahim, N. A., E-Zairy, W. R., & Eid, B. M. (2010). Novel approach for improving disperse dyeing and UV-protective function of cotton-containing fabrics using MCT-β-CD. *Carbohydrate Polymers*, *79*, 839–846.

Ibrahim, N. A., Eid, B. M., Hashem, M. M., Refai, R., & EL-Hossamy, M. (2010). Smart options for functional finishing of linen-containing fabrics. *Journal of Industrial Textiles*, *39*, 233–265.

Kang, I. S., Yang, C. Q., Wei, W., & Lickfield, G. C. (1998). Mechanical strength of durable press finished cotton fabrics. Part I. Effects of acid degradation and crosslinking of cellulose by polycarboxylic acids. *Textile Research Journal*, *68*, 865–870.

Lam, Y. L., Kan, C. W., & Yuen, C. W. (2011). Wrinkle-resistant finishing with dimethyloldihydroxyethyleneurea (DMDHEU)—The effect of co-catalyst. *Textile Research Journal*, *81*, 1419–1426.

Lu, H., Fei, B., Xin, J. H., Wang, R., & Li, L. (2006). Fabrication of UV-blocking nanohybrid coating via mini emulsion polymerization. *Journal of Colloid and Interface Science*, *300*, 111–116.

Montazer, M., & Afjeh, M. G. (2007). Simultaneous X-linking and antimicrobial finishing of cotton fabric. *Journal of Applied Polymer Science*, *103*, 178–185.

Wang, Q., & Hauser, P. J. (2010). Developing a novel UV protection process for cotton based on layer-by-layer self-assembly. *Carbohydrate Polymers*, *81*, 491–496.

Yang, C. Q., & Wei, W. (2000a). Mechanical strength of durable press finished cotton fabric. Part 2. Comparison of crosslinking agents with different molecular structures and reactivity. *Textile Research Journal*, *70*, 143–147.

Yang, C. Q., & Wei, W. (2000b). Evaluating glutaraldehyde as a nonformaldehyde durable press finishing agent for cotton fabric. *Textile Research Journal*, *70*, 230–236.